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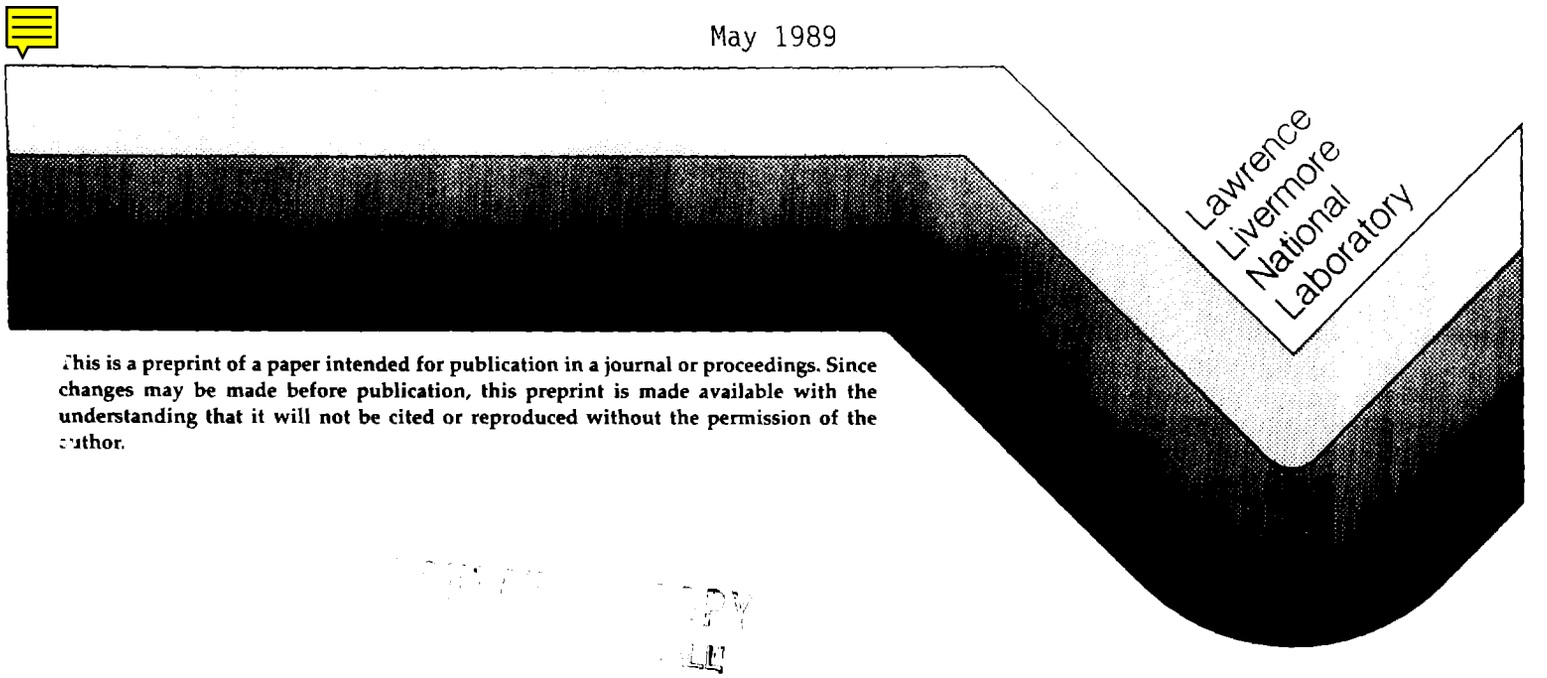

THE COMPLEXOMETRIC MICRODETERMINATION OF DIVALENT COPPER AND COBALT

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Divalent copper and cobalt can be determined on the microscale (0.5 to 6 mg) by titration with 0.01 N EDTA, using xylenol orange as indicator. For copper, acetate buffer must be used, while for cobalt hexamine is also satisfactory.

INTRODUCTION

Heretofore it was claimed that divalent copper and cobalt could not be determined complexometrically, using xylenol orange or methylthymol blue indicators, without a chelating additive such as 1,10-phenanthroline (1). This was based on the fact that cations with incomplete inner orbits form complexes stable with respect to substitution. Such complexes prevent complexometric determination of these elements. Addition of small amounts of 1,10-phenanthroline as an auxiliary complex-forming agent, according to Pribil, entirely suppresses this phenomenon.

We report in this work that microamounts of divalent copper and cobalt can be determined complexometrically using xylenol orange as indicator at room temperature without any additional chelating additives.

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EXPERIMENTAL

The titrant was an aqueous solution of 0.01 N EDTA, delivered from a 10-mL Machlett buret provided with a 1 liter reservoir. It was standardized against high-purity metallic copper dissolved in dilute nitric acid, or against an accurately prepared aqueous solution of reagent grade cupric sulfate pentahydrate. The indicator was a 0.2% (w/v) aqueous solution of the tetrasodium salt of xylenol orange.

A quantity of 0.5 to 6 mg of cupric ion (as a solution of reagent grade cupric sulfate pentahydrate) or of cobalt(II) (as a solution of reagent grade cobalt nitrate hexahydrate) were pipetted into a 50-mL beaker containing a stirring bar. The solutions were diluted to about 25 mL with deionized water. The pH was adjusted to 5.5 with solid sodium acetate trihydrate, using a pH meter. One drop of the indicator solution was added, and the samples were titrated with 0.01 N EDTA to a sharp color change from purple to yellow for cobalt, and from purple through grey to green for copper. The buret was graduated to 0.05 mL, and volumes could be estimated to 0.01 mL.

RESULTS AND DISCUSSION

Berndt and Sara (2) confirmed the work of Pribil (1) that it is not possible to titrate copper using xylenol orange (or methylthymol blue) vs EDTA, even at a higher temperatures (above ambient) in solutions buffered with hexamine. They suggested the use of sodium acetate as a buffer which, in conjunction with additives such as phenanthroline, permits the titration of copper in weakly acidic medium.

We have found that for microamounts of copper or cobalt, using 0.01 N EDTA as titrant, no other chelating additives are required and the titration is feasible at ambient temperature in an acetate-buffered medium at pH 5-6. At these low concentrations (4×10^{-4} to 4×10^{-3} M, or from 0.01 to 0.1 mmol per 25 ml of solution) the faint blue color of the cupric ion and the faint rose color of the cobalt(II) ion have only a minimal effect on the recognition of the endpoint. At extremely low concentrations (4 to 8×10^{-4} M) of copper, the color change if from purple through grey to yellow, while at somewhat higher concentrations the inherent blue color of the cupric ion will make the endpoint appear to be green. For higher concentrations of cupric ion ($>4 \times 10^{-3}$ M) recognition of the endpoint becomes more difficult because of the interference of the blue copper color.

The copper-chelating compounds, such as 1,10-phenanthroline or glycine, will enhance the blue color of the cupric ion, and thus are not recommended as additives in our procedure. We confirmed that hexamine cannot be used as buffer for the determination of copper. However, for the determination of microamounts of cobalt(II), sodium acetate as well as hexamine may be used. We recommend, however, that the same buffer be used throughout a standardization and analysis because of small differences in titrations (about 0.7%). In the case of cobalt(II), the color change at the endpoint is from purple to yellow.

The recoveries of 0.6 to 5.1 mg of copper and 1.1 to 5.3 mg of cobalt are presented in Tables 1 and 2. They averaged 99.90% for copper and 99.99% for cobalt. For a study of interferences the reader is referred to the excellent monograph by Pribil (3).

REFERENCES

1. Pribil, R. Talanta, 1959, 3, 91-94.

2. Berndt, W; Sara, J. Talanta, 1960, 5, 281-283.

3. Pribil, R., "Applied Complexometry," Pergamon Press, New York, 1982, p. 147-152, 160-164.

TABLE 1

Recoveries of Cupric Ion (as cupric sulfate pentahydrate)

mg taken	mg found	standard deviation	number of replicates	percent. recovery
0.642	0.637	0.003	4	99.22
1.283	1.285	0.006	4	100.16
2.567	2.569	0.002	4	100.08
3.208	3.206	0.004	4	99.94
3.850	3.848	0.004	4	99.95
5.133	5.134	0.003	4	100.02

TABLE 2

Recoveries of Co(II) (as cobalt nitrate hexahydrate)

mg taken	mg found	standard deviation	number of replicates	percent recovery
1.179	1.176	0.003	4	99.75
2.946	2.951	0.003	4	100.17
5.303	5.306	0.005	4	100.06

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